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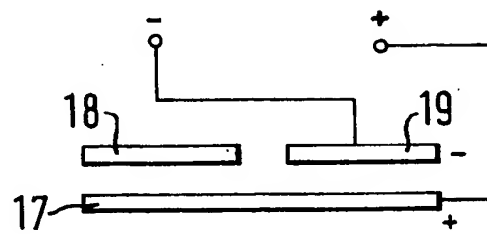
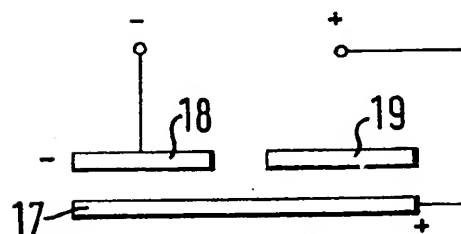
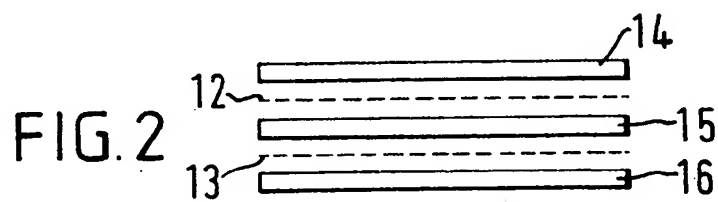
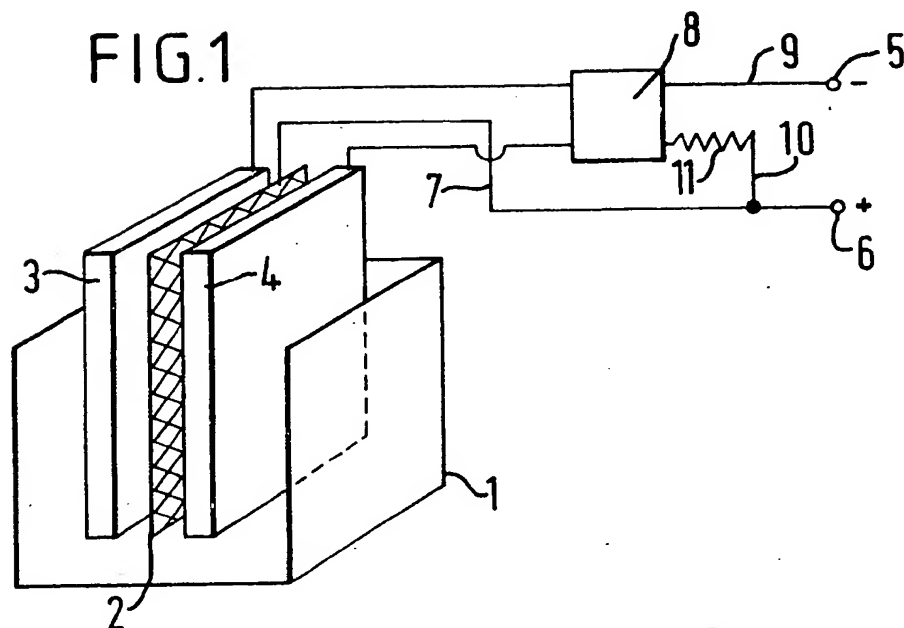
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(54) **Electrolytic cell**

(57) An electrochemical cell, particularly a hypochlorite cell, using a platinum group metal coated titanium anode, and two subsidiary electrodes, the subsidiary electrodes being in the form of a TiO_x material where x is in

the region 1.55 to 1.9, each subsidiary electrode being operated alternately as the cathode and during such periods when not operating as cathodes are connected as anodes to generate acid locally about the subsidiary electrode to clean the surface of deposits formed when it was operating as a cathode.

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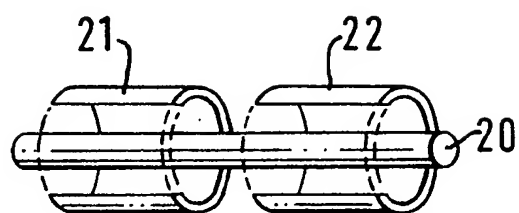


FIG. 5.

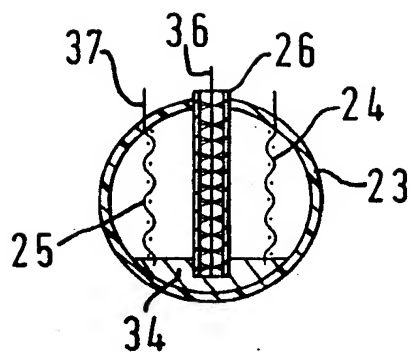


FIG. 6.

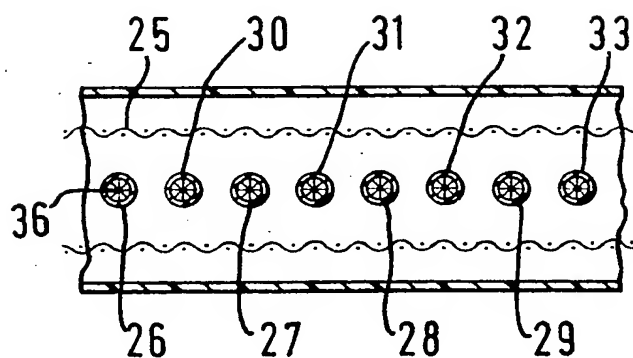


FIG. 7.

SPECIFICATION

Electrolytic cell

This invention relates to electrochemical cells and has particular reference to electrochemical cells for the electrolytic decomposition of chemical compounds.

In an electrolysis cell, such as a cell for the manufacture of sodium hypochlorite, there is essentially a series of anodes which are opposed to a series of cathodes. An electrolyte consisting of an aqueous sodium chloride solution is passed through the cell and is decomposed in the cell, the decomposition products recombining to form the required sodium hypochlorite. It is well known that impurities in the feed solution to the brine, particularly those impurities which are calcium- or magnesium-containing, can lead to physical scales being formed on the cathodes. In chlor-alkali cells generally it is often essential to take considerable precautions to purify the brine to very fine limits and at considerable cost to restrict the formation of scale. The scale which would otherwise be formed rapidly polarises the cathodes, raises the cell voltage and can even cause electrical shorting within the cell.

In sodium hypochlorite cells, however, the economics of the operation do not allow extensive liquor purification except in a few isolated cases, and in many plants the feed is natural seawater at whatever prevailing salinity and temperature exists at the feed inlet. Even for the smaller electrolyzers, sometimes used for the electrolysis of dilute brine in swimming pools, scale forms on the cathode and this seriously affects the functioning of the cell and ultimately can lead to total cell failure.

Amongst the impurities to be found in water such as seawater and the water in swimming pools are salts of magnesium and calcium. It will be appreciated, therefore, that the electrolyte passing through a sodium hypochlorite cell would contain magnesium ions and calcium ions. Around the cathodes in a sodium hypochlorite cell there will be formed a relatively highly alkaline solution as a result of hydrogen evolution at the cathode. This results in the formation of numerous OH^- ions around the cathodes. The OH^- ions chemically combine with the magnesium or calcium ions to form calcium or magnesium hydroxide which deposits as a scale upon the cathode.

It is necessary to remove the scale to permit the sodium hypochlorite electrolyser to operate efficiently. If the scale is not removed it can build up to such an extent that it will significantly reduce the electrical efficiency of the cell or even cause electrical shorting within the cell.

Although methods have been developed to reduce the formation of scale on the cathodes, namely the use of very high electrolyte flow rates through the cell, which, with appropriate design, give a turbulent flow, these methods result in higher pumping costs than would otherwise be required and result in lower sodium hypochlorite concentrations. Essentially three methods have

been developed to remove the scale formed on the cathodes. The first method involves the chemical treatment of the scale by simply dissolving it with a suitable acid. The cell is switched off and acid is poured in the cell to dissolve chemically the scale formed on the cathode. The second method is to rotate the electrodes and/or to mechanically scrape the scale of the cathode surface while the cell is in operation. The third and most popular method is to rely on water turbulence physically to prevent scale from adhering. A further variant on this latter method is to de-energise the cell and to pump a water/compressed air mixture through the cell channels to clean the cell. Relying on electrolyte turbulence has not in itself proved to be entirely satisfactory and acid washing is usually found to be necessary at some stage. Furthermore the action of turbulent water/compressed air mixture can cause physical erosion of the catalyst from the surface of the anodes.

A most useful method which has been developed involves reversing the current applied to the anodes and cathodes in the cell. Just as operation of the cathodes results in oxygen reduction and hydrogen evolution at the cathodes and a local increase in alkalinity as a result of the latter, so by comparison operation of the anodes results in some oxygen evolution as well as chlorine, the former resulting in local acidity developing in the vicinity of the anode. As such acid solutions can dissolve scale, the method essentially involves reversing the direction of current so that the electrode which has operated as a cathode and formed a scale is subsequently operated as an anode and the acid developed around the anode dissolves the scale formed whilst the electrode was acting as a cathode.

One known form of electrode for use with a sodium hypochlorite cell operated under current reversal conditions is a titanium electrode coated with a platinum group metal or a platinum group metal oxide. Unfortunately, however, such electrodes are very susceptible to corrosion when the current actually reverses. Furthermore operation of the electrodes as cathodes can result in hydriding of the titanium and undermining of the platinum group metal or platinum group metal oxide coating. Painted and fired coatings, such as ruthenium oxide based coatings, are more susceptible to corrosion than hard platinum metal coatings, such as electroplated coatings or metallurgically bonded layers of the type produced by co-extrusion. However, in order that the electrolyser may be simply cleaned by current reversal such rapid corrosion is accepted and the cathodes are thus cleaned by the formation of acidic conditions around them when they are connected as anodes during the period of current reversal. It will be appreciated that with such a cell each electrode is effectively negatively polarised for one portion of the time and positively polarised for the remaining part of the operation of the cell.

In US Patent No 4 088 550 there is described a method of removing cathodic deposits by periodic current reversal. However, instead of providing a

single cathode a pair of cathodes are provided, one of which operates as an active cathode whilst the other is connected anodically. When connected anodically acid is generated locally to

5 clean deposits from the electrode. Periodically the polarity of the electrodes is reversed. The material of the electrodes is said to be chosen from titanium, nickel and ferrous and nickel alloys such as Hastalloy C, which is a trade mark of Union
10 Carbide Corporation.

In US Patent No 4 306 952 there is described a similar cathode switching arrangement in which the switched electrode is cycled with a period between 80 and 330 minutes. The electrodes
15 which are switched are formed of graphite. Alternatively silicon, iron, stainless steel or magnetite are described as possible electrodes for this switched electrode.

Self-cleaning hypochlorite cells are frequently
20 used to purify water in swimming pools. Swimming pools tend to have a white or pale colour lining, such that any dirt collecting on the base of the pool rapidly becomes an eyesore. Furthermore, one of the virtues of chlorination of swimming pool water is not only that it disinfects
25 the water but also that it makes for a clearer, fresher looking water. Nickel based materials such as Hastalloy rapidly dissolve when made alternately anodic and cathodic turning the water
30 black in colour. Graphite tends to break up in operation and, although not dissolving, particles of black graphite collect on the pool floor and are unsightly. Silicon-iron tends to produce rusty water when alternately connected as an anode
35 and a cathode.

It is desirable, therefore, to produce an electrolytic cell which, when used as a swimming pool hypochlorite cell, does not cause such contamination of the water either by solution or by
40 detritus as to be unsightly.

By the present invention there is provided an electrochemical cell for the electrolytic decomposition of a chemical compound dissolved in water, the cell including an anode and at least
45 two subsidiary electrodes, the current supply to the cell being such that the anode is permanently connected in use as an anode and in that the subsidiary electrodes are operated intermittently as cathodes, one at least of the subsidiary
50 electrodes being in operation as a cathode when the cell is in operation, the other subsidiary electrode being cleaned of impurity deposits formed on its surface whilst operating as a cathode by acid conditions developed in the cell,
55 during operation of the cell, wherein the improvement comprises the subsidiary electrodes being formed of a material TiO_x where x is in the region 0.5 to 1.95.

The anode preferably comprises a titanium
60 substrate having an anodically active compound thereon. The anodically active compound may contain a metal or oxide chosen from the group platinum, iridium, palladium rhodium and ruthenium. The anodically active compound may
65 consist in its entirety of an oxide or of a metal or of

a mixture of metal and oxide chosen from said group.

The value of x in TiO_x is preferably in the region 1.55 to 1.95, and further preferably in the region
70 1.75 ± 0.1 . The acid conditions may be developed to clean the subsidiary electrode which has been operating as a cathode by connecting the subsidiary electrode as an anode so as to develop local acidity around the subsidiary electrode for
75 cleaning purposes. Alternatively the subsidiary electrodes may be spaced by a small distance from the anode such that the disconnection of the cathode permits it to exist in a region of high acidity and so be cleaned.

80 The subsidiary electrodes may be arranged in a line, with a pair of anodes disposed either side of the line. The subsidiary electrodes may be so connected that at a given time during operation of the cells anodes and cathodes alternate, the
85 distance between the subsidiary electrodes being less than the distance between the anodes and the subsidiary electrodes.

The TiO_x electrodes may be of any shape, including tubular, and may be operated at current
90 densities not exceeding 100 Amps/m².

The chemical compound may be sodium chloride.

The present invention further provides a method of operating an electrochemical cell for the decomposition of a chemical compound dissolved in water, the water containing impurities or minor additions that may be incorporated in alkaline cathode scales, wherein the cell is provided with an anode and at least two
100 subsidiary electrodes, operating the subsidiary electrodes intermittently and the subsidiary electrode not operating as the cathode being cleaned by acid conditions developed locally within the cell during operation of the cell, of
105 impurity deposits formed on its surface wherein the improvement comprises the subsidiary electrodes being formed of a material TiO_x where x is in the region 0.5 to 1.95.

The acid conditions may be developed by
110 operation of the scaled subsidiary electrode as an anode.

The main anode may be formed of titanium, niobium, tantalum or their alloys and have a coating of a platinum group metal or compound
115 formed on its surface by electroplating or by the metallurgical bonding of the metal to the titanium substrate. There may be provided alternatively an anode in which the platinum group metal is applied by a route involving painting a chemical
120 compound containing the platinum group metal onto the surface of titanium and firing the painted titanium in air or other preferred atmosphere to produce an anode. There may be provided an intermediate coating between the titanium and the platinum metal or compound, the intermediate
125 coating being provided for corrosion resistance purposes. The intermediate coating may be a tantalum metal or a non-stoichiometric tantalum or titanium oxide coating, or a mixture of such
130 oxides.

The cell may contain a plurality of anodes and subsidiary electrodes provided there are at least two subsidiary electrodes. It is important that the anodes be operated permanently as anodes and are not permitted to operate as cathodes.

An alternative material for the anode may be graphite or a platinum group metal or oxide coated TiO_x where x is in the region 0.5 to 1.95.

By way of example embodiments of the present invention will now be described with reference to the accompanying drawings, of which:

Figure 1 is a schematic view of an electrochemical cell in accordance with the present invention;

Figure 2 is a schematic view of a sodium hypochlorite generator for use in connection with the purification of swimming pools;

Figures 3 and 4 are schematic views of alternative forms of arrangement of anode and cathode;

Figure 5 is a schematic view of a rod and tube type electrochlorinator; and

Figures 6 and 7 are transverse and longitudinal sectional views of an alternate design of cell.

Referring to Figure 1 this shows schematically a typical set-up for a sodium hypochlorite generator, sometimes known as an electrochlorinator, of the type used to generate sodium hypochlorite for the disinfection of swimming pools. The cell 1

contains a titanium mesh anode 2 and a pair of TiO_x subsidiary electrodes 3, 4. The TiO_x subsidiary electrodes are formed of a TiO_x material where x is approximately 1.75. The anode 2 is formed from a titanium mesh having on its surface

a layer of a tantalum oxide, and on the tantalum oxide a layer of painted and fired platinum or platinum-iridium anodically active coating. An electrical current supply is provided which is a direct current, there being a negative pole 5 and a

positive pole 6. It can be seen that the positive pole 6 is permanently connected via line 7 to the anode 2. The subsidiary electrodes 3 and 4 are, however, connected to an automatic time polarity

switch 8. The feed of electricity to the switch 8 is both negative via line 9 and positive via line 10 and bias or step down resistance 11. By means of the automatic time polarity switch 8 the current supply to the subsidiary electrodes 3 and 4 can be as follows.

i For a first period of time, typically 30 minutes, the subsidiary electrode 3 is connected via switch 8 directly to negative pole 5. The subsidiary electrode 4 is, however, connected via switch 8 to a positive supply of electricity via bias 11 and line 10. If the operation of the subsidiary electrode 4 is initially ignored and the electrochemical reaction is considered as taking place between anode 2 and the subsidiary electrode 3 which is acting as a cathode, after a certain period of time a scale of magnesium hydroxide or calcium hydroxide will begin to deposit on the cathode 3, as a result of the local alkalinity formed around the cathode 3 and the reduction of water to form OH^- ions around the cathode 3. The OH^- ions chemically combine with

the calcium or magnesium ions to form insoluble calcium or magnesium hydroxide which deposits on the cathode 3 as a scale.

ii After the 30 minute period has expired the automatic time polarity switch 8 reverses the polarity of subsidiary electrodes 3 and 4. Subsidiary electrode 4 then operates as a conventional cathode to generate sodium hypochlorite in the conventional manner as a result of a reaction between anode 2 and subsidiary electrode 4 acting as a cathode on the dilute brine solution contained in cell 1. By comparison, however, the subsidiary electrode 3 is now biased as an anode, albeit at a relatively low current density compared to the main anode 2. Typically the current density at the anode 2 would be in the region 0.5 kA/m^2 to 2 kA/m^2 (depending on the electrolyte resistivity) and the operating current density at the cathode would be in a similar region. However, the current density applied to the subsidiary electrode 3 when it is made anodic would be of the order of 80 to 100 A/m^2 . At this low level of anodic polarity the subsidiary electrode acting as an anode would produce some local acidity as a consequence of oxygen evolution, and this acidity is found to dissolve chemically (not electrochemically) the scale formed on the subsidiary electrode 3 when it was operating as a cathode in the first portion of the cycle.

It will be noted that the anode 2 operates continuously as an anode and may, therefore, be operated under an ideal regime, and because the current is not reversed at the anode it has a long life and a high efficiency. Similarly as the subsidiary electrodes 3 and 4 are maintained substantially clean they operate efficiently also. The low anodic current density applied to each of the subsidiary electrodes when it is connected as an anode in the cleaning phase is such that no significant damage occurs to the subsidiary electrode during that phase.

Overall it has been found that the current efficiency in a cell similar to that illustrated in Figure 1 approaches 80% to 85% in seawater, and rather less in the much more dilute brine found in swimming pools, whereas the current efficiency in cells which are cleaned by conventional mechanisms is often very much lower.

It will be appreciated that the cell illustrated in Figure 1 is a schematic cell, the only requirement for the cell being that there is a supply of sodium chloride solution, i.e. brine, dilute or otherwise, to the cell and the sodium hypochlorite product is removed from the cell for use in disinfecting water in swimming pools or power station cooling systems or ship-borne heat exchangers.

Illustrated in Figure 2 is a schematic version of a modified form of cell in accordance with the present invention. In the arrangement illustrated in Figure 2 there are two anodes 12, 13 which are sandwiched between three subsidiary electrodes 14, 15 and 16. The electrical arrangement would be such that the anodes 12 and 13 would be operated continuously whereas the cathodic

current would be applied alternately to the central subsidiary electrode 15 and subsequently to the external pair of subsidiary electrodes 14 and 16.

Although it is probably preferred that the subsidiary electrode, which is not operating as a cathode during the operation of the cycle when the alternate subsidiary electrode is in operation, should be connected as an anode, it is possible that mere physical closeness to the main anode may enable the subsidiary electrode not in operation to be acid cleaned by the acid conditions surrounding the main anode.

Referring to Figures 3 and 4 these show in schematic form an arrangement in which the main anode 17 is in permanent operation. The subsidiary electrode 18 is shown in Figure 3 as operating opposite the anode and sodium hypochlorite will be generated between the anode and the subsidiary electrode.

Referring to Figure 4 this shows that the anode 17 continues to operate, whereas the main cathode is subsidiary electrode 19. As a result of the physical proximity of the subsidiary electrode 18 to the anode 17 local acidity generated around the anode 17 may well be sufficient physically to clean the subsidiary electrode 18.

The preferred material for the subsidiary electrodes is the titanium sub-oxide TiO_x where x has a value of approximately 1.75. Particular advantages of this material are:

- i a low solubility for H_2 and therefore the material is stable as a cathode over long periods of operation
- ii it does not react with cathodically generated hydrogen to form a titanium hydride
- iii that it possesses significant electrocatalytic behaviour as an anode and allows a significant anodic current to be passed.

Such a material is essentially a ceramic material and may, therefore, most easily be fabricated by ceramic technology. It may be produced as tubes and rods as well as in flat plate form. Illustrated in Figure 5 is a form of construction in which the anode takes the shape of a central rod 20 and the subsidiary electrodes are tubular members 21 and 22. The subsidiary electrodes are operated alternately in the same manner as is illustrated in Figure 1 or Figures 3 and 4.

With such a design, the electrodes have very few sharp corners, which tend to act locally as current raisers, and high local current can be detrimental to TiO_x material.

The design illustrated in Figures 6 and 7 shows a suitable form of cell for use as a hypochlorite cell for a swimming pool electrolyser. The tube or pipe 20 is of plastics material and forms part of the ducting for the water path in the water circulation system of the swimming pool. Located in the tube 23 is a pair of spaced titanium mesh anodes 24, 25 which are disposed in parallel lines as can be seen more clearly in Figure 7. Between the titanium mesh anodes is a series of subsidiary electrodes 26 to 33. The lower ends of the mesh electrodes 24 and 25 and the tubular electrodes

26 to 33 are embedded in a epoxy potting compound 34. Connection to the tubular electrodes 26 to 33 is by means of a wire brush connector 36 which extends into the tubular electrodes. Connection to the mesh anodes 24 and 25 is by means of an external power connection 37.

The tubular electrodes 26, 27, 28 and 29 are connected to one source of electricity and the tubular electrodes 30, 31, 32 and 33 are connected to an alternate source. The platinised titanium mesh 24 and 25 is always connected as an anode and the electrodes 26 to 29 are connected alternately as anodes and cathodes. Thus the switching is between tubular electrodes 26 to 29 and tubular electrodes 30 to 33.

The advantage of the design illustrated in Figures 6 and 7 over the design illustrated in Figure 2 is that when, for example, electrode 30 is an anode it is close to cathodes 26 and 27 and thus electrically there is an easy line of communication. By comparison when the electrode 15 is connected as an anode the electrodes 14 and 16 have to be electrically connected through the existing anode 12. There is, therefore, a difficulty in the anode 15 seeing the cathodes 14 and 16.

A further advantage with the design illustrated in Figures 6 and 7 is that the subsidiary electrodes 26 to 33 can be placed closer together than the gap between those electrodes and the anodes 24 and 25. As a result of this it is possible to modify the current flow between the subsidiary electrodes to get adequate current flow for cleaning purposes. It is preferred that the gap between the subsidiary electrodes is less than the gap between the subsidiary electrode and the permanent anodes.

Furthermore the design illustrated in Figures 6 and 7, by using tubular TiO_x electrodes, enables smooth designs of electrodes to be used which, by having no rough edges or corners, reduces the chances of electrode degradation in use.

It will further be appreciated that the exact form of the subsidiary electrodes is optional. They could take the form of rods spaced from mesh anodes or any other suitable form as required.

The preferred material of the cathode, namely the uncoated TiO_x material, where x is approximately 1.75, is ideally used in circumstances where relatively low power efficiencies at the cathode can be tolerated, e.g. in low capacity electrochlorinators as used for disinfecting swimming pool water. Thus in a swimming pool sodium hypochlorite generator the total current consumption is only approximately 150 W and the system has the advantage of being one which is permanently operable with the minimum of maintenance.

In some circumstances, however, such as sodium hypochlorite generators for use in the disinfection of seawater and the cooling supplies for power stations, the amount of sodium hypochlorite to be generated is so high that the cathode inefficiencies become significant. In such

a circumstance it may be desirable to apply a thin layer of platinum, preferably as a platinum black to the TiO_x material to improve the power efficiency. By keeping the switching of polarity to a low frequency the wear rate on the platinum can be minimised.

It will be appreciated that the description given above has concentrated on the use of the cell as a sodium hypochlorite cell. However, the cell may also be operated to produce sodium chlorate, since this can be effected by operating at higher temperatures ($80-105^\circ\text{C}$) and at a very slightly greater level of acidity (pH 6.5 to 6.8). The TiO_x material is resistant to operation at high temperatures and in acid solutions.

It will be understood that in addition to use of the cell in aqueous sodium chloride solutions the cell could be operated with sodium bromide as a feed solution to form sodium bromate.

It will further be appreciated that there are many advantages to the cell set out above as compared to the prior art.

i As the cathode scale is continually removed the cell may be operated uninterruptedly for a long period of time without any maintenance being required.

ii The simplicity of the design means that it could be manufactured in a wide range of sizes, from very small units suitable for swimming pools to large plant of the type used in power stations.

iii The simplicity of the cell facilitates servicing which can be of great importance when used on ships, oil platforms or in remote locations.

iv The electrolyte flow rates within the cell do not need to be high to reduce scaling, thus reducing pumping costs and, more importantly, giving a higher efficiency in hypochlorite formation.

v With the exception of the electrolyte pump there are no moving parts and thus very little to go wrong. The solid state electronics required to switch the current are of a conventional form.

vi The lack of solubility of the TiO_x material and the fact that it does not break up in use means that there are no black deposits of significance formed by operation of the cell, which black deposits may be unsightly when the cell is a hypochlorite cell used as a swimming pool electrolyser.

CLAIMS

1. An electrochemical cell for the electrolytic decomposition of a chemical compound dissolved

in water, the cell including an anode and at least two subsidiary electrodes, the current supply to the cell being such that the anode is permanently connected in used as an anode and in that the subsidiary electrodes are operated intermittently as cathodes, one at least of the subsidiary electrodes being in operation as a cathode when the cell is in operation, the other subsidiary electrode being cleaned of impurity deposits formed on its surface whilst operating as a cathode by acid conditions developed in the cell, during operation of the cell, wherein the improvement comprises the subsidiary electrodes being formed of a material TiO_x where x is in the region 0.5 to 1.95.

2. An electrochemical cell as claimed in Claim 1 in which the anode comprises a titanium substrate having an anodically active compound thereon.

3. An electrochemical cell as claimed in Claim 1 in which the value of x in TiO_x is in the region 1.55 to 1.95.

4. An electrochemical cell as claimed in Claim 3 in which the value of x in TiO_x is in the region 1.75 ± 0.1 .

5. An electrochemical cell as claimed in Claim 1 in which the acid conditions are developed to clean the subsidiary electrode which has been operating as a cathode by connecting the subsidiary electrode as an anode so as to develop local acidity around the subsidiary electrode for cleaning purposes.

6. An electrochemical cell as claimed in Claim 5 in which there is provided a plurality of subsidiary electrodes arranged in a line with a pair of anodes disposed either side of the line.

7. An electrochemical cell as claimed in Claim 6 in which the subsidiary electrodes are so connected that alternately each is an anode and a cathode at a given time, and the distance between the subsidiary electrodes is less than the distance between the anodes and the subsidiary electrodes.

8. An electrochemical cell as claimed in Claim 1 in which the subsidiary electrodes are spaced by a small distance from the anode such that the disconnection of the cathode permits it to exist in a region of high acidity and so be cleaned.

9. An electrochemical cell as claimed in Claim 2 in which there is provided an intermediate coating of tantalum or tantalum oxide between the titanium anode and its anodically active coating.

10. An electrochemical cell as claimed in Claim 1 in which the TiO_x electrodes are operated at a current density not exceeding 100 Amps/m².